The conversion of **1** to **2** represents the simplest intraresin reaction reported to date. It proceeds without a significant change in cross-link density and resin composition and is amenable to direct kinetic analysis. Further studies based on this system are in progress.

Acknowledgment. We are grateful to Dr. Stephen Mazur (E. I. du Pont de Nemours and Co.) for helpful discussions.

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(18) In principle, the extent of kinetic isolation in cross-linked polymers should depend upon the chemical rate and the distribution of encounter frequencies. While 30% of the sites in **1** become isolated, faster chemical reactions using similar supports should result in even greater isolation; slower reactions should yield fewer isolated sites.

Tris[phenyl(difluorophosphino)amino]phosphine ($P[N(C_6H_5)PF_2]_3$), a Novel Tridentate Strong π-Acceptor Ligand Forming Cage Chelates. Crystal Structure of the Chelate Complex $P[N(C_6H_5)PF_2]_3Mo(CO)_3$

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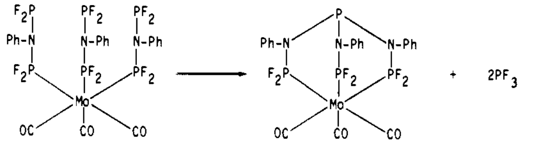
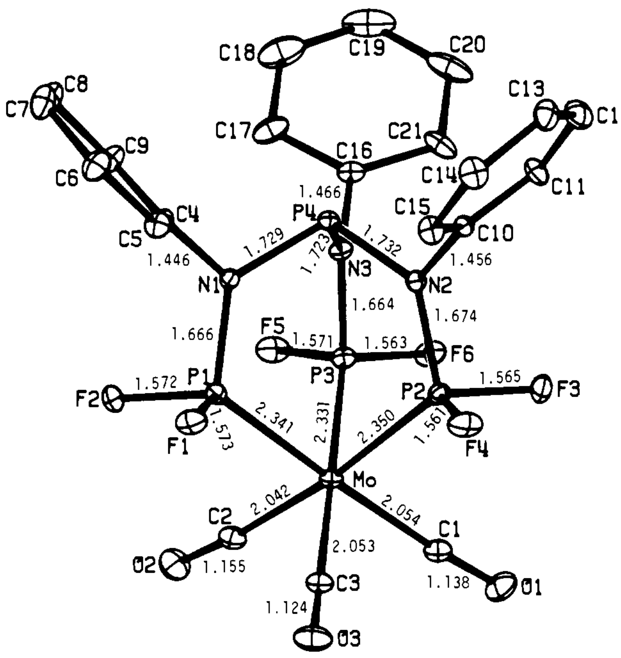
Received April 9, 1981
Revised Manuscript Received July 1, 1981

Chelating strong π-acceptor ligands are of interest in connection with the stabilization of complexes of transition metals in low oxidation states that exhibit unusual chemical properties,[2] including the important one of activity in homogeneous catalytic reactions. We report the first example of a tridentate chelating strong π-acceptor ligand containing three σ-donor, π-acceptor PF_2 groups and describe the novel bicyclo[2.2.2]octane-like cage structure of the complex $P[N(C_6H_5)PF_2]_3Mo(CO)_3$ (**1**) in which the ligand has been identified. The new tridentate ligand, tris[phenyl(difluorophosphino)amino]phosphine, is formed by an unprecedented reaction, the elimination of PF_3 from *N,N*-bis(difluorophosphino)aniline ($C_6H_5N(PF_2)_2$), which occurs when *fac*-$(CH_3CN)_3Mo(CO)_3$ reacts with the latter to yield **1** as an unexpected product. We suppose that the mechanism of formation of the ligand $P[N(C_6H_5)PF_2]_3$ involves an initial step in which $C_6H_5N(PF_2)_2$ reacts as a monodentate ligand with *fac*-$(CH_3CN)_3Mo(CO)_3$ to yield *fac*-$[C_6H_5N(PF_2)_2]_3Mo(CO)_3$ (**2**) by simple ligand substitution. Then the proximity of the three uncomplexed PF_2 groups of the three mutually cis $C_6H_5N(PF_2)_2$ ligands in **2**, coupled with the tendency to form six-membered chelate rings, facilitates the elimination of PF_3 to form the tridentate ligand in place in **1**.



2 1

A solution of *fac*-$(CH_3CN)_3Mo(CO)_3$ was generated by boiling 4.0 g (15 mmol) of $Mo(CO)_6$ in 75 mL of acetonitrile for 24 h. This solution was stirred with 5.0 g (22 mmol) of $C_6H_5N(PF_2)_2$[3] for 2 days at 40–45 °C. Solvent was then removed in vacuum, and the residue was extracted with pentane. Concentration and cooling of the pentane extract gave 1.0 g of a white crystalline metal carbonyl complex (**1**), mp 229–231 °C, sublimation temperature 125 °C (0.001 mm). Since the stoichiometry and structure of **1** could not be determined by conventional analytical and spectroscopic methods, the product was subjected to single-crystal X-ray diffraction analysis.



P1-Mo-P2	86.8(1)	P1-Mo-P3	88.5(1)	P2-Mo-P3	85.3(1)
C1-Mo-C2	93.9(3)	C1-Mo-C3	88.9(3)	C2-Mo-C3	92.1(3)
C1-Mo-P2	89.6(2)	C2-Mo-P1	89.7(2)	C3-Mo-P1	90.4(2)
C1-Mo-P3	92.1(2)	C2-Mo-P3	88.7(2)	C3-Mo-P2	93.9(2)
C1-Mo-P1	176.3(2)	C2-Mo-P2	173.2(2)	C3-Mo-P3	178.7(2)
Mo-C1-O1	176.6(6)	Mo-C2-O2	175.0(6)	Mo-C3-O3	178.5(6)
Mo-P1-N1	118.0(2)	Mo-P2-N2	117.1(2)	Mo-P3-N3	116.9(2)
Mo-P1-F1	117.6(2)	Mo-P2-F3	118.6(2)	Mo-P3-F5	120.5(2)
Mo-P1-F2	120.4(2)	Mo-P2-F4	120.9(2)	Mo-P3-F6	119.1(2)
N1-P1-F1	102.4(2)	N2-P2-F3	101.0(2)	N3-P3-F5	100.8(2)
N1-P1-F2	100.5(2)	N2-P2-F4	100.5(2)	N3-P3-F6	101.3(2)
F1-P1-F2	93.5(2)	F3-P2-F4	94.5(3)	F5-P3-F6	94.0(2)
N1-P4-N2	103.0(2)	N1-P4-N3	104.2(2)	N2-P4-N3	104.1(2)
P1-N1-P4	123.8(3)	P2-N2-P4	124.1(3)	P3-N3-P4	125.7(3)
P1-N1-C4	122.3(4)	P2-N2-C10	122.4(4)	P3-N3-C16	119.4(4)
P4-N1-C4	113.4(4)	P4-N2-C10	113.3(4)	P4-N3-C16	114.9(4)

Figure 1. The structure of $P[N(C_6H_5)PF_2]_3Mo(CO)_3$, showing all important bond lengths (Å) and valence angles (deg). The estimated standard deviations of the bond lengths are Mo–P, 0.002; Mo–C, 0.008; P–F, 0.004; P–N, 0.005; N–C, 0.007; C–O, 0.007 Å. The atoms are represented by their thermal ellipsoids of 10% probability.

The product **1** forms monoclinic crystals by slow evaporation of a diethyl ether solution. The space group is $P2_1/c$, uniquely determined by the systematic absences. From diffractometric data, the unit-cell parameters are $a = 8.683$ (1) Å, $b = 28.218$ (7) Å, $c = 15.338$ (2) Å, and $\beta = 118.12$ (1)°. There are four molecules per cell. The structure was determined from intensity data recorded with an automatic diffractometer using filtered Mo Kα radiation and the θ–2θ step-scan technique to the limit of $2\theta = 50°$. Absorption corrections were applied. The solution for the structure was obtained by the heavy-atom method, and refinement was done by the full-matrix least-squares method. Anisotropic thermal parameters were adjusted for all 38 nonhydrogen atoms of an asymmetric unit of formula $P[N(C_6H_5)PF_2]_3Mo(CO)_3$. The hydrogen atoms were not located. The final discrepancy index $R(F)$ is 0.052, on the basis of 3079 reflections having $F_{obsd}^2 > 2\sigma(F_{obsd}^2)$.

The structure of **1**, shown in Figure 1, is that of an octahedral *fac*-$L_3Mo(CO)_3$ complex. The tridentate ligand, $P[N(C_6H_5)PF_2]_3$, has its three PF_2 groups linked to the Mo atom so as to form a cage molecule with interlocking six-membered rings, similar to bicyclo[2.2.2]octane. As one of the bridgehead atoms of the cage, the central phosphorus atom of the tridentate ligand is not directly bonded to the Mo atom, which is the other bridgehead atom.

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[1] Visiting scientist from Department of Chemistry, Carleton College, Northfield, MN 55057.

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Although it contains no crystallographic symmetry element, the complex molecule, even including the three phenyl groups, comes close to displaying the $3m$ symmetry it would be expected to have in isolation (see the bond-length and -angle data in Figure 1). The coordination polyhedron about the molybdenum atom is distorted slightly from an ideal octahedron. For example, the three P–Mo–P angles are 86.8 (1), 88.5 (1), and 85.3 (1)° instead of the ideal 90°, probably as a necessary consequence of closing the rings of the cage.

The observed chemical and spectroscopic properties of the new chelate complex **1** can readily be reconciled with the structure found. Thus, elemental analyses[4] are consistent with the stoichiometry $P[N(C_6H_5)PF_2]_3Mo(CO)_3$. The proton-decoupled phosphorus-31 NMR spectrum in dichloromethane solution exhibits the following two resonances: (1) a resonance assigned to the three equivalent PF_2 groups, centered at δ 157.1 and split into a 1197-Hz triplet by the strong phosphorus–fluorine coupling; (2) a resonance assigned to the central phosphorus atom, centered at δ 101.3 with no major splitting. The infrared spectrum exhibits frequencies ν(CO) at 2041 and 1988 cm^{-1}, consistent with a *fac*-$L_3Mo(CO)_3$ complex containing relatively strong π-acceptor ligands.[5]

The Mo–P bond lengths, averaging 2.343 Å, and the Mo–C bond lengths, averaging 2.050 Å, provide striking evidence of the strong π-acceptor character of the PF_2 groups. The Mo–P bonds are among the shortest ever observed for trivalent phosphorus ligands bound to molybdenum, and the Mo–C bonds are among the longest ever observed for carbonyl groups similarly bound. These bond lengths are essentially identical within experimental error with the corresponding lengths 2.369 (10) and 2.063 (6) Å in $Mo(CO)_5PF_3$[6] and 2.063 (3) Å in $Mo(CO)_6$,[7] from gas-phase electron-diffraction analysis in each case. Some other relevant comparisons are available in ref 8. Since the Mo–C bond order in $Mo(CO)_6$ may be assigned[5,9] a value of 1.5, it follows then from the bond-length data that the Mo–C and Mo–P bond orders in $Mo(CO)_5PF_3$ and **1** must all be about 1.5. We conclude, then, that each ligating group of the tridentate ligand in **1** is about as strong a π acceptor as the CO or the PF_3 molecule.[10]

A few other features of the molecular structure deserve brief comment. The F–P–F angles, averaging only 94.0°, are remarkably small in comparison with the angle 97.8 (2)° in PF_3[11] and the angle 99.5 (5)° in $Mo(CO)_5PF_3$.[6] The average P–F bond length, 1.568 Å, is close to the lengths 1.570 (1) and 1.557 (4) Å in PF_3 and $Mo(CO)_5PF_3$, respectively. The average of the three P(4)–N bond lengths is greater by 0.060 Å than the average of the other three P–N bonds.

Acknowledgment. The portion of this research performed at the University of Georgia was partially supported by the U.S. Air Force Office of Scientific Research under Grant AFOSR-75-2869. The portion of this research performed at the Oak Ridge National Laboratory was sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corporation.

Supplementary Material Available: Lists of atomic coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(4) Anal. Calcd for $C_{21}H_{15}F_6MoN_3O_3P_4$: C, 36.5; H, 2.2; N, 6.1; M_r, 691. Found: C, 35.8, 36.3; H, 2.0, 2.3; N, 6.0, 6.0; M_r, 659 in benzene.

(5) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702. The related compound *fac*-$Mo(CO)_3(PCl_3)_3$ exhibits frequencies ν(CO) at 2040 and 1991 cm^{-1}.

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(10) Cotton[5] has concluded from an approximate calculation of the force constant of the C–O bond in *fac*-$Mo(CO)_3(PF_3)_3$ that PF_3 is a considerably stronger π acceptor than CO. A similar conclusion has been reached from analysis of photoelectron spectra of PF_3, $Ni(PF_3)_4$, and $Pt(PF_3)_4$ by: Green, J. C.; King, D. I.; Eland, J. H. D. *J. Chem. Soc., Chem. Commun.* **1970**, 1121.

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Synthesis of Nitrogen-Containing Polycycles on the Basis of a New Method of *o*-Quinone Methide Imine Generation

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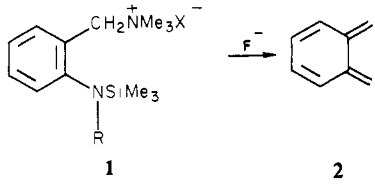
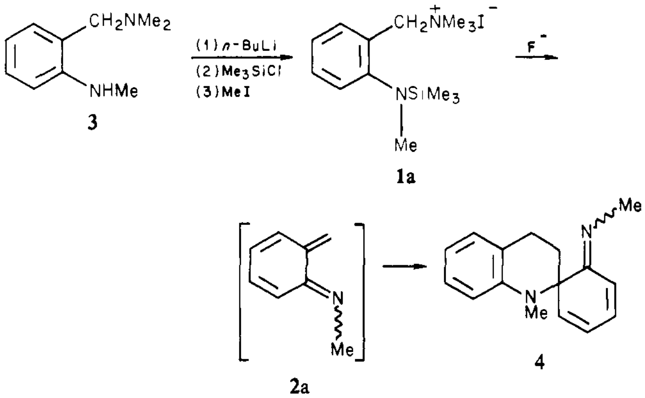
Received April 1, 1981

Intramolecular Diels–Alder reactions have been widely used for syntheses of polycyclic ring systems with stereocontrol.[1] Recently, we reported[2] a stereoselective synthesis of steroid frameworks on the basis of the mild generation of *o*-quinodimethanes, in which [*o*-[α-(trimethylsilyl)alkyl]benzyl]trimethylammonium halides are treated with fluoride anion at room temperature.

It was now found that [*o*-[(trimethylsilyl)alkylamino]benzyl]trimethylammonium halide (**1**) also underwent the fluoride anion induced 1,4-elimination under mild conditions to generate *o*-quinone methide *N*-alkylimine intermediate (**2**).[3] Described herein are the syntheses of nitrogen-containing polycycles based on this methodology for the generation of N-substituted *o*-quinone methide imine (**2**). When [*o*-[(trimethylsilyl)methylamino]benzyl]trimethylammonium iodide (**1a**),[4] prepared by N-silylation via lithiation at the nitrogen of [*o*-(methylamino)benzyl]dimethylamine (**3**) followed by quaternization with methyl iodide, was treated with CsF or tetrabutylammonium fluoride in acetonitrile at room temperature, spirotetrahydroquinoline derivative **4** was isolated as a yellow liquid (chromatography on silica gel) in 77% yield. The structural assignment of **4**[5] is based on the spectral data [IR (neat) 1650, 1610, 1585 cm^{-1}; NMR ($CDCl_3$ with Me_4Si) δ 2.0 (m, 2 H), 2.62 (s, 3 H), 2.8 (m, 2 H), 3.30 (s, 3 H), 6.0–7.4 (m, 8 H)] and hydrogenolysis of **4** on Pd/C affording 1,2-bis[*o*-(methylamino)phenyl]ethane.[6]





Spirotetrahydroquinoline derivative **4** may be derived from [4 + 2] cyclodimerization of the *o*-quinone methide imine (**2a**).[3b]

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(4) **1a**: NMR ($CDCl_3$ with Me_4Si) δ 0.08 (s, 9 H), 2.87 (s, 3 H), 3.13 (s, 9 H), 4.66 (s, 2 H), 7.2–7.8 (m, 4 H).

(5) Compound 4 turns brown and decomposes on standing in air.

(6) 1,2-Bis[*o*-(methylamino)phenyl]ethane: mass spectrum, *m/e* (relative intensity) 240 (M^+, 20), 172 (7), 121 (11), 120 (100), 118 (9), 93 (7), 91 (37), 77 (13), 65 (20); high-resolution mass spectrum, *m/e* 240.1628 (calcd 240.1626).

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